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EFFECT OF STABILIZERS ON GOLD SENSITIZATION

by

Douglas E. Corbin

B.S. University of California at Santa Barbara

(1974)

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science in the School of  
Photographic Arts and Sciences in the  
College of Graphic Arts and Photography  
of the Rochester Institute of Technology

May, 1982

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CERTIFICATE OF APPROVAL

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MASTER'S THESIS

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ROCHESTER INSTITUTE OF TECHNOLOGY  
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Douglas E. Corbin

Author

# EFFECT OF STABILIZERS ON GOLD SENSITIZATION

by

Douglas E. Corbin

Submitted to the Photographic Science and Instrumentation Division in partial fulfillment of the requirements for the Master of Science degree at the Rochester Institute of Technology.

## ABSTRACT

Previous work has shown evidence that some emulsion stabilizers can prevent rearrangement of adsorbed silver sulfide to a photographically active form. Full gold plus sulfur sensitization may be achieved by simultaneous introduction of the sensitizers or by adding gold after sulfur sensitization. As gold sensitization of an already optimally sulfur-sensitized emulsion may instead involve a direct chemical reaction, the effect of stabilizers on gold sensitization may not parallel their effect on sulfur sensitization. The stabilizers 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene and 1-phenyl-5-mercaptotetrazole retard but do not prevent gold sensitization in a sulfur sensitized emulsion. This may suggest that gold sensitization does not involve a rearrangement or other secondary process with which a stabilizer could interfere.

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## INTRODUCTION

The history of silver halide photography has been characterized by an unending search for increased sensitivity. Often this search falls into the realm of chemical sensitization. Chemical sensitization, in the modern sense, is a chemical treatment of the emulsion which usually follows its precipitation. This treatment increases the efficiency of latent image formation and confers increased sensitivity which is normally independent of the wavelength of the exposing radiation. Until recently, the selection of gelatins, which contained naturally occurring chemical sensitizers as a consequence of their processing, was of prime importance. These sensitizers were either sulfur-containing substances (usually sodium thiosulfate) which produced sulfur sensitization and/or reducing substances which produced reduction sensitization. These natural substances were often enhanced by the addition of synthetic sensitizers, but the nature of the gelatin was still of great importance. Today, with the availability of modern purification methods, such as large-scale deionization, coupled with greater knowledge and control of the variables in the manufacture of gelatin, the use of inert gelatins containing extremely

low levels of sensitizers and restrainers is widespread. Inert gelatins require that sensitizing substances be added to produce chemical sensitization. Sodium thiosulfate and thioureas are commonly added to emulsions to produce sulfur sensitization. The use of gold salts as chemical sensitizers was discovered by Koslowsky in 1936.<sup>1</sup> Gold sensitization is not usually applied alone because it produces low contrast and is generally used in conjunction with sulfur sensitization (referred to as sulfur plus gold, or S+Au sensitization). Sulfur plus gold sensitization is mainly used on camera speed silver iodobromide emulsions. Combined sulfur and gold sensitizations can yield a speed increase of 2 to 2.5 times that obtainable with sulfur sensitization alone. While S+Au sensitization is normally achieved by adding both substances at the start of digestion, useful gold sensitizing effects can be obtained by the use of gold as a final addition in after-ripening.<sup>2</sup> Harbison and Spencer<sup>3</sup> state that, "Successive additions of solutions of sodium thiosulfate and sodium dithiocyanatoaurate (I) can be used also." However, the reference<sup>4</sup> for that statement makes no mention of the addition of sodium thiosulfate solution but instead uses an active gelatin digestion followed by the gold solution. If sodium thiosulfate is the active sulfur sensitizer in that gelatin, then the two statements can be reconciled. Harbison and Hamilton<sup>5</sup> showed that the

sensitometric effects of an S+Au sensitization could be duplicated by hypersensitizing (prior to exposure) a sulfur sensitized emulsion with an aurous thiocyanate solution. The use of gold after sulfur sensitization is important in the present work.

## I. Sulfur Sensitization

In the process of sulfur sensitization with sodium thiosulfate, the sensitizer is adsorbed, according to a Langmuir isotherm, on the silver halide surface. The adsorbed thiosulfate then decomposes to form silver sulfide.<sup>6</sup> It has been shown that no unique quantity of silver sulfide is formed at optimum digestion. In addition, the rate of sensitization and the amount of silver sulfide present at optimum speed increases with increasing thiosulfate concentration. Indeed, Spracklen<sup>7</sup> found that using thiosulfate as the sensitizer, no unique amount of  $\text{Ag}_2\text{S}$  is formed at optimum sensitivity. Considering that sometimes 1/10 of the sulfide formed can result in similar sensitivity when compared with experiments where much larger amounts of sulfide are produced, leads Spracklen to postulate, "...that the sulphide is in at least two different conditions, in one of which it has no effect on sensitivity. The centrifuging experiments show that this cannot be simply a question of a part of the sulphide formed in the bulk gelatin, where it could have no photographic effect... However, the observation that the more slowly silver sulphide

is formed (at least with respect to changes in thiosulfate concentration and  $pAg$ ), the more efficient it is as a sensitizer, does suggest the idea that the formation of these two types of silver sulphide may be consecutive rather than simultaneous; i.e., that the silver sulphide as first formed does not act as a chemical sensitizer... and that it is only some subsequent change which confers chemical sensitizing properties. Using Dickinson's hypothesis,<sup>61</sup> this idea would mean that all the silver sulphide is originally formed as discrete molecules, and that subsequently some of these molecules aggregate to form specks." Work by Bassett and Dickinson,<sup>8</sup> using thiourea as the sulfur sensitizer, showed that fog and sensitivity centers produced with low levels of sensitizer (longer digestion times until optimum) were much more prone to bleaching in chromic acid than centers produced by high levels of sensitizer (shorter digestion times until optimum). In a second experiment, the fog centers were treated with a gold thiocyanate solution prior to the bleaching treatment. Fog produced by the low levels of sensitizer was enhanced but the fog from the higher levels of sensitizer was markedly reduced. These results may be explained if the fog (and sensitivity) centers consist of both silver and silver sulfide. The relative proportions of these two components are related to the quantity of sulfur sensitizer added to the emulsion. Thus,

another interpretation of a two stage mechanism of sulfur sensitization is that the silver sulfide does not become an efficient sensitizer until it is associated with a small quantity of metallic silver. A two stage sensitization mechanism is also suggested by the work of Stevens<sup>9</sup>. He found that addition of a simple soluble sulfide to an emulsion had little sensitizing effect but, that upon heating, sulfur sensitization was obtained that was comparable to that observed from sodium thiosulfate.

## II. Gold Sensitization (S+Au)

Though the function of gold in chemical sensitization is still obscure, results of experiments helping to define its role have become available in recent years. Gold solutions may be used to latensify latent images produced in emulsions which are not gold sensitized. The effect is greatest in the high intensity exposure region. This was first shown by B. H. Carroll in a paper by James, Vanselow, and Quirk.<sup>10</sup> The same reference also shows that a gold latensified latent image is much more resistant to oxidative bleaching and concludes that latent image silver is replaced by gold. In latensification (a post exposure treatment), gold is apparently acting to reduce the number of atoms necessary to catalyze development.<sup>11,12</sup> Hautot and Sauvenier<sup>13</sup> showed that the latent image formed in emulsions given S+Au sensitization was more resistant to oxidation treatment than the latent image formed in emulsions with only sulfur sensitization. Spracklen<sup>14</sup> extended this work using mercuric chloride bleaches. It was observed that

the proportion of latent image, in a S+Au sensitized emulsion, which is bleach resistant increases with increasing exposure duration or with post exposure light latensification, but not with delays of up to several hours between exposure and development. The conclusion is that the resistance to bleaching, corresponding to a higher percentage of elemental gold, is almost certainly conferred during the actual exposure. In addition, neither centrifuging the emulsion and reconstituting with fresh gelatin nor adding colloidal Carey Lea silver (as a gold scavenger) affected the bleach resistance of the latent image. This implied that the gold which enters the latent image must be firmly bound to the grain surface even before exposure. In addition, the experiments suggest that the gold responsible for gold sensitization is probably an ionic form and that during exposure at least some of these ions are reduced and built into the latent image.

Spencer, Brady, and Hamilton<sup>15</sup> and Spencer and Atwell<sup>16</sup> showed that gold latensification could greatly reduce or eliminate high intensity reciprocity law failure (HIRF) of a sulfur sensitized emulsion. They found, that with high intensity exposures, sulfur sensitized emulsions had an increased number of development centers (vs. lower intensity exposures) which had a random spatial distribution. The dispersity of the development centers was the apparent cause of the HIRF. Gold latensification eliminated the HIRF and increased the number of countable development specks



but it did not change the Poisson form of the speck distribution resulting from the high intensity exposure. Their gold treatment also greatly narrowed the wide spread of development induction times present with high intensity exposure. The results infer that the presence of gold makes smaller latent image specks developable. If these development centers coincide with the original sensitivity specks, and since gold latensification has many of the properties as gold sensitization, it may be that the gold in S+Au sensitization adds directly to or may be located physically very near the sulfide specks produced by the sulfur sensitizer.

The sensitivity increase attributable to gold latensification would appear to be due to an improvement in the developability of small or subdevelopable latent image specks as the treatment is applied after exposure. However, work by Harbison and Hamilton<sup>11</sup> has shown that sensitization above that obtainable with gold latensification is possible if gold is present in a sulfur sensitized emulsion prior to exposure either by gold sensitization (S+Au) or by gold hypersensitization. In addition, it was found that the auxillary gold treatments (latensification and hypersensitization) had no material effect on a S+Au sensitized emulsion. Their results indicate a dual function for gold used in chemical sensitization: 1) gold reduces the number of atoms required for a latent image center capable of catalyzing development and prevents the onset of HIRF

and 2) gold stabilizes the atom state of silver over what is provided by sulfur alone, which favors increased efficiency of latent image nucleation and produces overall sensitization. These conclusions of Harbison and Hamilton are in agreement with the microwave photoelectron lifetime data of Kellogg.<sup>17,18</sup> Her results show that sulfur sensitization decreases free lifetime in a silver bromide emulsion at room temperature. The sulfur sensitivity centers are thus apparently trapping photoelectrons. However, there is no change in the lifetimes when S+Au sensitization is used vs. that of sulfur sensitization, when the amount of sulfur deposited is kept equal. This indicates that gold does not increase electron trap depth as has been previously proposed in the literature.

Hillson and Adam<sup>19</sup> suggest that most of the increase in sensitivity conferred by gold sensitization is due to gold nuclei being more efficient development centers than silver nuclei of the same size. They found that there is a significant underpotential for the deposition of silver on gold, using cyclic voltammetry, vs. the potential needed for depositing silver on silver. Farnell and Solman<sup>12</sup> have found further evidence that gold is involved in latent image formation for its part in chemical sensitization. On 7 out of 8 AgBr emulsions prepared in different ways but having mean grain areas of approximately  $1\mu\text{m}^2$ , the internal speed was lower for optimum sensitization with

S+Au than for optimum sensitization with sulfur alone. The combined sensitization increases the probability of trapping electrons at the grain surface and thus improves the efficiency of formation of surface latent image. Farnell and Solman<sup>20</sup> later re-examine their results in light of suggestion by Faelens<sup>21</sup> and conclude that the sensitivity conferred by gold is due to an increase in the number of sensitivity centers per grain resulting from an increase in the rate of deposition of sulfide in the presence of gold. Competitive effects due to the increased number of centers would be compensated by the latensifying effect of gold sensitization and the increase in efficiency of formation of surface silver. Because there is no increase in fog on optimum sensitization with S+Au, they suggest that there is a reduction in the average size of a sensitivity center. Mechanical deformation data on the 8 emulsions is also given. Mechanical stress apparently introduces disorder into the grains which increases the efficiency of internal image formation and desensitizes the surface image. Without exception, the desensitization was significantly less with optimum S+Au sensitization than with optimum sulfur sensitization alone. This is evidence that gold is involved in latent image formation and that trapping of electrons at surface sites (a topographic effect) is more efficient with S+Au than with sulfur sensitization only.

Locker<sup>22</sup> corroborates the finding that the rate of sensitization and fog formation is increased in S+Au sensitization over that found with sensitization using an equivalent amount of sulfur sensitizer alone. However, the kinetics of formation of fog and sensitivity centers are both first-order with respect to thiosulfate whether or not gold is present. In addition, it was determined that there was not apparent induction time for fog or sensitivity center formation with S+Au sensitization. With sulfur only there was an induction time for fog center formation but not sensitivity center formation. Locker also presents evidence that, when normalized to zero development time, the energies of activation for formation of fog and sensitivity centers are the same for either S+Au or sulfur alone in chemical sensitization. However, the activation energy ( $E_a$ ) values are almost double for the fog and sensitivity centers produced from S+Au sensitization over sulfur sensitization. This doubling may indicate formation of sensitizing entities with a different chemical composition and a change in the kinetic route by which the fog and sensitivity centers are produced. The similarity in  $E_a$  values for fog and sensitivity centers, detected upon short development times, suggest that the two types of centers are either identical or closely related, whether S+Au or S-only sensitization is used.

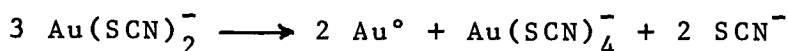
The fog reducing properties of gold sensitization can be clearly seen from Faelens' work<sup>21</sup> in which a gold thiocyanate complex is added to an emulsion already ripened into fog with sulfur sensitizer alone. The fog is dramatically reduced. The converse is also true. Addition of a labile sulfur compound to an emulsion ripened into fog with a gold thiocyanate complex reduces fog as well as sensitivity.<sup>23</sup> Faelens and others postulate that gold sulfide is formed in these cases and is less efficient as a fog or sensitivity center than other species. Earlier experiments of Faelens<sup>21,24</sup> showed that colloid silver sulfide nuclei were much more effective as physical development centers than gold sulfide nuclei, but that gold nuclei were more effective than silver nuclei. Shuman and James<sup>25</sup> examined the catalytic activity of Ag, Au, Ag<sub>2</sub>S, Au<sub>2</sub>S and Au<sub>2</sub>S<sub>3</sub> in silver physical development. It was found that the relative activities depend on the developing agent used. Generally, the metal sulfides were less effective than the metals in initiating development. The sulfides also showed, with one exception, definite development induction times. Reaction rates for three developing agents with the nuclei were as follows:

Metol	Ag > Au >> Ag <sub>2</sub> S > Au <sub>2</sub> S > Au <sub>2</sub> S <sub>3</sub>
Hydroquinone	Au > Ag <sub>2</sub> S > Ag >> Au <sub>2</sub> S <sub>3</sub> > Au <sub>2</sub> S
Phenidone	Au > Ag >> Au <sub>2</sub> S > Ag <sub>2</sub> S = Au <sub>2</sub> S <sub>3</sub> = 0

The increase in emulsion sensitivity caused by ripening with a sulfur sensitizer under usual sensitizing conditions is a rather gradual process which goes through a maximum. Faelens<sup>26</sup> has duplicated this behavior on gelatin-free AgBr sols using sodium thiosulfate as the sensitizer. Corresponding to increasing sensitivity, a gradual decrease in pH is also seen as hydrogen ion is a by-product of the sensitization reaction. However, under the same conditions except using a gold thiosulfate complex containing the same quantity of thiosulfate, an almost instantaneous increase in sensitivity and decrease in pH was observed. The difference in the rate of increase in photographic sensitivity is important. It may indicate that the presence of gold is having a catalytic influence on the breakdown of thiosulfate to sulfide as hydrogen ion is thought to be a by-product of the breakdown reaction.

The nature of the sensitivity center in gold sensitization is of interest in the present work. The lower catalytic activity of gold sulfide was noted previously. In gelatin-silver halide systems, the reducing properties of the gelatin are never totally eliminated. Typical afterripening conditions of heating the emulsion for tens to hundreds of minutes at a very low level of soluble excess halide might suggest the possibility of reduction of gold sensitizer by gelatin to produce elemental gold (and/or elemental silver). However, in work on gelatin-free silver bromide sols, Faelens<sup>23,24</sup>

demonstrated good sensitization with gold thiocyanate complexes (no labile sulfur). Oxidation of the sol prior to sensitization to remove any traces of reducing agent did not prevent sensitization. This may be evidence of the dismutation of gold (I) into elemental gold and gold (III). Faelens postulates that in the emulsion:



The only other plausible form of gold present in chemical sensitization might be gold (I) ions. Mitchell<sup>27</sup> and others have presented information indicating that  $\text{Au}^+$  can diffuse rapidly in AgCl and AgBr. Comparing the ionic radii of silver and gold<sup>28</sup> indicate a reasonable similarity: the radius of  $\text{Ag}^+$  is 1.26 Å and the radius of  $\text{Au}^+$  is 1.37 Å. These radii are probably much larger than the real values in silver halides due to a considerable covalent component in the bonding. However, if both radii are reduced by a similar factor by bonding in the crystal, the percentage difference would be small.  $\text{Au}^+$  ions could join the population of interstitial  $\text{Ag}^+$  ions in the silver halide emulsion grain. In this form, the gold would not be localized in a sensitivity center as would elemental gold.

The most recent experiments of Faelens<sup>29,30</sup> indicate that elemental gold (and, possibly, elemental silver) and gold sulfide (and, possibly,  $\text{Ag}_2\text{S}$  or the mixed sulfide) are both formed in S+Au sensitization and are responsible

for the sensitizing and fog reducing characteristics of this type of sensitization respectively. Using radiotracer techniques, it was shown that gelatin binds with approximately 90% of the gold from an added gold thiocyanate complex in an experimental emulsion. When the same quantity of gold thiocyanate is added concurrently with an equivalent amount of thiosulfate ion, the level of gold remaining in the gelatin is reduced to about 25% over a 60 minute period. The 60 minute period parallels the increase in sensitivity. If the gold complex is added simultaneously with a small amount of reducing agent (thiourea dioxide), no change is seen in the 90% of the gold bound by the gelatin. However, an increase in sensitivity occurs which is of the same magnitude as that from S+Au sensitization. In order to reduce the amount of gold bound by the gelatin, very large amounts of reducing agent must be added. This treatment also results in gross fog. Under the conditions of the experiment, adding either the gold complex or the reducing agent alone resulted in very little sensitivity increase. The reducing agent alone caused a buildup of fog. The fog was decreased and the sensitivity greatly increased when both the gold complex and reducing agent were used together. The conclusions which may be reached are that gold sensitization, in the presence of a small quantity of reducing agent and in the absence of labile sulfur compounds, results in an extremely small amount of gold reaching the silver halide crystal, not detectable by tracer techniques,



and an increase in sensitivity comparable to ordinary S+Au sensitization. Fog was somewhat greater on extended afterripening with Au plus reducing agent compared with that from S+Au. In the presence of thiosulfate anion, the quantities of gold reaching the grain are much larger and probably coincide with the gradual production of mainly gold sulfide and a very small quantity of elemental gold. The gradual disappearance of gold from the gelatin phase is not related to slow adsorption of thiosulfate, as Spracklen has shown adsorption of thiosulfate to be very rapid.<sup>6</sup> Also, in the case of S+Au sensitization, fog was formed at a much slower rate. This is also an indication of the presence of gold sulfide. In addition, aurous sulfide is a very insoluble compound:  $pK_{sp} > 13$ .<sup>31</sup> Faelens' experiments indicate that elemental gold is the sensitizing entity in the absence of labile sulfur compounds and that much less than the amounts actually added are required on the grain surface. The presence of both elemental gold and gold sulfide on the grain is not precluded by these results for the case of S+Au sensitization. A further point worthy of consideration is that much earlier work by Faelens and Travernier<sup>32</sup> showed that a suspension of silver sulfide could be converted to gold sulfide by the addition of gold salts.

Using flash induced, transient, differential absorption techniques in the visible spectrum, S.H. Ehrlich<sup>33</sup> has produced some new evidence regarding the nature of the

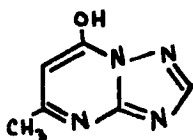
centers produced by chemical sensitization. Sulfur sensitization of a small grain AgBr emulsion using sodium thiosulfate produced two discrete chemical species. Two possibilities might be:  $\text{Ag}_2\text{S}$  and unreacted  $\text{S}_2\text{O}_3^{=}$  or  $\text{Ag}_2\text{S}$  (molecular) and  $\text{Ag}_2\text{S}$  (aggregated). AgBr grains sensitized with  $\text{KAuCl}_4$  shows spectra due to  $\text{Au}^\circ$  with cluster diameters less than  $15\text{\AA}$  (limit of electron microscopy) or less than 10 atoms of  $\text{Au}^\circ$  along the linear surface diameter of the cluster. Comparison of the spectra from S+Au sensitization with those from S-only and Au-only shows the disappearance of the bands observed with S and Au alone and the formation of a new chemical species at the sulfur or gold sites. Ehrlich's interpretation indicates that the possibilities for the new chemical species are  $\text{Ag}_3\text{AuS}_2$ ,  $\text{AuAgS}$  and  $\text{Au}_2\text{S}$ . Combining photoionization potential data with the transient absorption spectra allows the energy levels due to the chemical sensitizing centers on AgBr to be positioned. From this Ehrlich concludes that AgBrI grains, treated with S+Au sensitizers, can acquire 3 functional responses at the surface (a) electron trapping by unfilled molecular levels (surface states); the greater the number of unfilled states,  $\text{S+Au} > \text{S}$ , the greater the probability of electron trapping, (b) hole trapping by the  $E_{\text{ho}}$  levels of S+Au when valence band holes are injected into an iodide site, the level of which lies below that of S+Au, and (c) a recombination center - an inefficiency in the latent image formation process.

### III. Stabilization

Silver halide photographic emulsions are perishable entities in that their original sensitometric properties change upon aging; the rate of change being dependent on factors such as temperature and humidity. Efforts to stabilize these properties have been ongoing since the advent of photography. Carroll, Hubbard, and Kretchman<sup>34</sup> proposed that changes which occur on storage may be considered as a slow continuation of chemical sensitization (going past an optimum to produce fog). The earlier practice of using excess halide ion only, prior to coating, was somewhat successful because the rate of chemical sensitization (with sulfur compounds) is dependent on the silver ion concentration in the emulsion and the excess halide thus lowered that concentration according to the solubility product equation (raised the  $pAg$ ).<sup>7</sup> Organic compounds were being tested by the middle 1920's as possible stabilizers of sensitometric properties. A stabilizer, as defined by Duffin,<sup>35</sup> must either prevent the continued formation of the sensitizing entity from excess chemical sensitizer still present, or prevent further quantities of the sensitizing entity, formed on storage, from becoming effective photographically. Generally, stabilizers are compounds which form slightly soluble silver salts by replacement of hydrogen on their secondary amine and/or mercapto functional groups. Examples include benzotriazoles, benzimidazoles,

mercaptotetrazoles and so on. The compounds which form very insoluble silver salts, such as some mercaptotetrazoles, are usually the most strongly adsorbed and retard development. Others, like the azaindenes, are weakly adsorbed and do not retard development at high pH values.

A real breakthrough came in 1935 when Birr discovered that 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (hereafter called TAI) was an effective stabilizer which caused no speed loss. The structural formula and synonyms are shown below:<sup>36</sup>



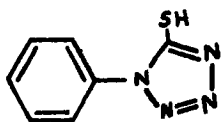
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (TAI);

5-methyl-7-hydroxy-1,3,4-triazaindolizine;

5-methyl-[1,2,4]triazolo[1,5-a]pyrimidin-7-ol

TAI, which is usually added at the end of chemical sensitization (by sodium thiosulfate), markedly stabilizes the sensitometric properties of the emulsion without inhibition of development.<sup>37</sup>

Many other stabilizers are based on sulfur-containing groups, 1-phenyl-5-mercaptotetrazole (hereafter called PMT) being a well known example. These sulfur compounds are effective in much smaller concentrations but they often inhibit development with an attendant speed loss in some types of emulsions.<sup>38</sup>



1-phenyl-5-mercaptotetrazole (PMT)

PMT also exists in a tautomeric form called 1-phenyl-2-tetrazoline-5-thione. The aqueous solubility of the silver salt of PMT is about six orders of magnitude smaller than that of TAI.  $K_{sp}$  for Ag(PMT) is  $6.31 \times 10^{-17}$  and for Ag(TAI) is  $3.16 \times 10^{-11}$ .<sup>39</sup> Also, stabilizers which are bound to silver predominantly by a sulfur-silver bond (PMT) generally are much more strongly adsorbed to silver halides (possible chemisorption) than those bound through a nitrogen-silver bond (TAI). Most often, the adsorption of stabilizers to silver halide is directly related to their silver salt solubilities. It is well known in the literature that PMT is much more strongly adsorbed to silver halides than TAI. However, the solubility of Ag(TAI) is also pH dependent. In alkaline (pH > 8.5) developer solutions, it usually does not inhibit development or function as an antifoggant. Rising and Carroll<sup>40</sup> found that TAI did function as an antifoggant in an Amidol developer and in a ferro-EDTA developer in the pH range of 6.0 - 8.5. To reach the same (low) percentage surface coverage on silver halide grains, a much larger amount of TAI must be in solution, in equilibrium with the adsorbed TAI, than with PMT. PMT can stabilize in amounts as low as 10 to 20 mg/mole AgX whereas the weakly adsorbed TAI is used in quantities of approximately 1 g/mole AgX.<sup>41</sup>

Berendsen, Faelens, and Dupain-Klerkx<sup>42</sup> showed that TAI and PMT could suppress photographic activity during sensitization with sodium thiosulfate, but, at the same sensitizer concentrations, did not stop silver sulfide formation. This and the fact that no unique quantity of silver sulfide is formed at optimum sensitivity indicates that some process is occurring to convert it to a photographically active form. This was the impetus for the work by Gingello, McIntyre, and Carroll.<sup>43,44,45</sup> To avoid the complication of adsorbed sodium thiosulfate first reacting to form silver sulfide, they first showed that a soluble sulfide could sulfur sensitize to a speed equivalent to that obtainable with sodium thiosulfate after Stevens.<sup>9</sup> The reaction of a soluble sulfide with silver halide is immediate and forms silver sulfide directly. However, a definite digestion period is still required to achieve sensitivity, indicating that some change in the silver sulfide is taking place. They showed that this digestion could be stopped immediately after the addition of stabilizers (TAI) in amounts which cause only a partial coverage of the grain surface. The conclusion is that silver sulfide may be redistributed to active sites on the grain surface to cause sensitization. Presumably, these are the same sites to which the stabilizer can adsorb to block sensitivity at partial grain surface coverage. If a physical relocation of the sulfide takes place, the stabilizer might prevent it by either adsorption

to the active site or to the silver sulfide itself. Alternately, or in addition to a migration, silver sulfide may aggregate into particles large enough to become electron traps. An efficient stabilizer might prevent the aggregation. Since Wood<sup>46</sup> showed that stabilizers are more strongly adsorbed to silver sulfide than to silver halide, the stabilizer, adsorbed to the initial form of silver sulfide, may prevent its rearrangement into a particular form (particular crystal habit, epitaxial structure, etc.) which is capable of electron trapping during exposure. Hamilton and Brady<sup>47</sup> have shown that stabilizers, adsorbed to the surface of emulsion grains, markedly reduce dark conductance and the concentration of interstitial silver ions. If the sensitivity increase due to sulfur sensitization is accompanied by the formation of silver metal, referred to earlier in connection with Bassett and Dickinson's<sup>8</sup> experiments, a probable source of the silver is from mobile interstitial silver ion,  $Ag_i^+$ . If adsorbed stabilizers reduce the  $Ag_i^+$  concentration, then the increase in sensitivity would be slowed or stopped. Frieser<sup>48</sup> and Herz<sup>49</sup> have mentioned that TAI strongly restrains AgBr recrystallization and stabilizes the grain surface. This would discourage sulfide incorporation into the silver halide substrate and conceivably prevent sensitization.

This work complements that of Gingello, MacIntyre, and Carroll<sup>43,44,45</sup> which showed evidence that stabilizers prevented (TAI) or slowed (PMT) the redistribution of silver sulfide on emulsion grains to a photographically active form or to active sites on the silver halide surface. Gold sensitizers may be incorporated into the emulsion by a direct chemical reaction with little or no necessity for rearrangement. The action of a given stabilizer on gold sensitization may not be analogous to its action on sulfur sensitization. As gold is almost always used in conjunction with sulfur commercially, the interaction of stabilizers with gold sensitization alone was examined when that gold was applied to an emulsion already sensitized to optimum speed with sulfur. Experimental information thus obtained may be of value in helping to elucidate the nature of the sensitizing entity and the mechanism of gold sensitization.

The experimental hypothesis was that the widely used stabilizer, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (TAI), would stop the reaction of gold with a sulfur sensitized emulsion when interposed between the sulfur and gold sensitizations. A neutral, single jet, silver iodobromide emulsion was precipitated, afterripened to a relatively constant (with digestion time) optimum speed with sodium thiosulfate, then gold sensitized with auric chloride, and stabilized with TAI and PMT at various times throughout the gold finish. Measurements of photographic sensitivity



were used to follow the presence and magnitude of the effects of the stabilizers on the process of gold sensitization.

## EXPERIMENTAL

The laboratory work was roughly divided into two major areas: preparation of an emulsion with known properties and performing gold sensitization and stabilizer experiments on that emulsion. The specific aim of the experiments was to show whether or not gold will cause sensitization in the presence of stabilizers in a fully sulfur sensitized emulsion. In order to isolate this particular effect, or the lack thereof, it was necessary to show that a number of other processes were not operating in the experiments. An example of this was testing to show that significant sensitization is not due to the gelatin itself. After the chemical experiments, the film was sensitometrically exposed, given standard processing, and evaluated on a densitometer. Photographic speed was the primary measurement for the observation of experimental effects, although contrast was also noted.

A neutral, single jet, silver iodobromide emulsion containing about 3 mole percent iodide was used for the work. This type of emulsion normally contains a polydisperse grain size distribution of twinned octahedra. It was chosen because it is representative of a commercial camera negative emulsion on which S+Au sensitization and stabilizers are normally used. In addition, this emulsion type is known to chemically sensitize well.<sup>50</sup> To minimize emulsion-to-emulsion variability, it would have been desirable to precipitate all of the emulsion needed at one time. However, the largest

batch which could be conveniently handled with the available facilities was an emulsion containing 0.2 moles of silver halide. During precipitation, about a 10 mole percent excess of potassium bromide was included. To allow for physical ripening after precipitation, the bromide concentration was raised to 0.075N. The use of 7% phthaloyl gelatin obviated the need for the older, cumbersome practice of shredding the emulsion into noodles for washing. It was the only gelatin present during the precipitation at an average concentration of about 0.7%. Prior to making the emulsion, the isoelectric point of the phthalated gelatin had to be determined. The isoelectric point is that condition where the number of positive and negative charges on the functional groups of the gelatin are equal. In the case of phthalated gelatin, its water solubility reaches a minimum at that point also. Knowledge of the location of this point allowed the correct amount of acid to be added, at the end of precipitation and Ostwald ripening to coagulate the emulsion. Prior to their use in the emulsion, the potassium bromide and potassium iodide were titrated against standard silver nitrate solution so that known amounts could be used.

For precipitation, the silver nitrate solution, at room temperature, was added from a glass separatory funnel through glass capillary tubing in approximately 30 minutes

to a 2 liter stainless steel beaker in a constant temperature water bath at 65°C. The silver nitrate was added directly into the mixing head of a high speed, homogenizing mixer immersed in the halide-gelatin solution. After an Ostwald ripening period using additional potassium bromide, the emulsion was flocculated with acid and refrigerated. After washing with distilled water, the coagulum was redispersed, in portions, with additional inert bone gelatin, sodium hydroxide solution (to bring the pH to 6.2 to 6.5 at 40°C), and dilute potassium bromide solution (to bring the pAg to 8.8 at 40°C) to produce the primitive emulsion used in the sensitization experiments. See Table 1 for the exact specifications of the emulsion making operation. Table 2 lists the results of the analyses of the chemicals used in the experiments.

The emulsion was further characterized by obtaining electron micrographs as shown in Figure 1. It can be seen that the emulsion does largely consist of rounded doubly-twinned octahedra. A grain size frequency distribution by the technique of electrolytic grain size analysis (EGSA)<sup>51,52</sup> was obtained (Figure 2). The number weighted mean diameter was 0.34 $\mu$  with a coefficient of variation of 40.3. The electron micrographs and EGSA were supplied by the Polaroid Corporation, Waltham, Massachusetts.

Following sensitization and stabilization experiments on the primitive emulsion (described in detail later), the

emulsion samples were coated on Kodak portrait (thick) triacetate sheet film base with a gelatin pelloid backing. Coatings were applied using the RIT emulsion sample coating machine. A 5 x 18 inch piece of film base was attached to a fixed platen via vacuum and emulsion was coated by extrusion through a slot head on a moving carriage. After coating, cold water was run through the platen causing the emulsion to chill-set. After setting up, the coated film was dried in a light tight cabinet with moving air at room temperature. Coating conditions were adjusted so that emulsion was extruded at a rate which closely matched the rate of travel of the carriage so as to minimize ripples, etc. and to obtain the desired silver coating weight. The aim silver coating weight was approximately  $6000 \text{ mg Ag}^\circ/\text{m}^2$ . This value was high enough to produce a layer of emulsion sufficiently heavy so that some fluctuation in coverage would not have a significant effect on the toe speed of the emulsion.

Experimental coatings were given sensitometric exposures using an Eastman Kodak Model 101 Process Control Sensitometer. A Kodak No. 2 step tablet was used to modulate the exposures. This type of tablet gives a nominal change of  $0.15 \log H$  units per step. To guard against the possibility of failure of the tungsten lamp used in the sensitometer, two new lamps were matched for spectral output to a Kodak-supplied standard

lamp using an EG&G Spectroradiometer. Exposure time provided by the sensitometer was 0.2 seconds. Output with no attenuators in the light path was 1700 lux (meter candles).

Standard processing was given using a vacuum bottle processor said to provide excellent agitation and reproducibility.<sup>53</sup> Kodak DK-50 developer was used because of its good capacity, because it is primarily a surface image developer, and because it is also representative of developers used in actual practice. Following development, Kodak SB-1 stop bath and Kodak F-6 acid hardening fixer were used to complete the processing. Uniformity of processing was verified by processing many replicates of Kodak Panatomic-X film which had been exposed in the sensitometer.

Processed sensitometric film strips were evaluated by measuring visual diffuse densities on a calibrated Macbeth TD-504 densitometer. Photographic speeds reported are the change in log exposure needed to produce a density of 0.10 over base plus fog density relative to an unsensitized control emulsion.

## RESULTS

## I. Heat Treatment of the Primitive Emulsion (Gelatin Test)

Prior to chemical sensitization, the response of the emulsion to heating was observed. This was a check on the inertness of the gelatin system to be sure that significant sensitivity was not imparted by the gelatin over the time and temperature ranges used for the sensitization experiments. In all experiments, the primitive emulsion carried its full complement of gelatin (phthalated gelatin for precipitation and inert gelatin for coating). In all cases, the total gelatin was present, at the level of 250 g per mole of silver. As can be observed from Table 3, the emulsion gained only 3/8 of a stop (0.12) in speed after being heated for 300 minutes at 55°C. This was better than acceptable.

## II. Determination of Sulfur Sensitizer Level

Some past experience with this kind of emulsion indicated that a reasonable level of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) to use for sulfur sensitization was about  $8.0 \times 10^{-5}$  moles  $\text{Na}_2\text{S}_2\text{O}_3$  per mole Ag. However, for the purposes of these experiments, it was desired to have an optimum speed over a broad digestion time plateau so that the emulsion would not be materially increasing in speed when gold sensitizer and stabilizers were added in subsequent experiments. For those reasons, two lower levels,  $2.5 \times 10^{-5}$  and  $5.0 \times 10^{-5}$

moles  $\text{Na}_2\text{S}_2\text{O}_3$  per mole Ag were examined. The sensitizer solution was made up immediately before use for all sensitizations using  $\text{Na}_2\text{S}_2\text{O}_3$  to insure full potency. For the lower level 0.040 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$  per liter of sensitizing solution was used. 0.080 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$  per liter was used for the higher level. Table 4 shows the results of the sulfur afterripenings. A speed/fog plot of the same results is shown in Figure 3. The level of  $5.0 \times 10^{-5}$  moles  $\text{Na}_2\text{S}_2\text{O}_3$  per mole Ag was picked because it had a reasonable speed plateau, a higher optimum speed, and a shorter time to optimum than the lower level.

### III. Determination That TAI Stops Sulfur Sensitization

Though the bulk of emulsion 2 was used up trying to find some preliminary Au sensitizer level which would provide a speed increase over sulfur alone and to cure some coating uniformity problems, two near-replicate tests showed TAI prevents any further sensitivity after its addition. See Table 5. Another kind of test which was more definitive is also shown in the table. TAI was added to the primitive emulsion and given 5 minutes to equilibrate. Sulfur sensitizer was added and the emulsion was heated for an additional 120 minutes and no increase in sensitivity was observed.

### IV. Determination of Useful Speed Plateau for Sulfur Sensitization

Since a number of procedural changes had been made after the first sulfur sensitizer test, a new speed/fog



vs. digestion time series was run to determine the useful range of times available for adding Au sensitizer (a useful range where there is no material increase in sensitivity due to sulfur). There is an appropriate "window" between 105 minutes and 150 minutes of digestion. Speed increases less than 1/2 stop and fog remains low. One of the procedural differences which appeared to have a significant effect was crossing over from Kodak Wratten No. 96 gelatin neutral density filters to Kodak Inconel on glass neutral density filters in the sensitometer. Speeds were lower with the No. 96 filter even though each filter had been read on a densitometer. A check of a Kodak publication on neutral density attenuators<sup>54</sup> indicated significantly more far blue - near UV absorption in the No. 96 filter vs. the Inconel. Since the emulsion was only sensitive in that range, the spectral transmission of the filters may have explained some of the difference. All subsequent experiments were run with the 1.2 N.D. Inconel filter to minimize any variability. See Table 6.

#### V. Determination of Appropriate Gold Sensitization

Sources in the literature indicate that approximately a one stop increase in speed may be achieved using S+Au sensitization over that obtained using only sulfur.<sup>55</sup>

In addition, it is indicated that S+Au may be present from the start of the afterripening or that Au may be added after

digestion with sulfur.<sup>56,57</sup> A survey of levels of gold used in the literature was made in the proposal for this thesis. A typical level was  $4 \times 10^{-6}$  moles Au/mole AgX.<sup>56</sup> Sensitizers were either auric chloride or the monovalent dithiocyanate complex. To keep experiments as uncomplicated and straightforward as possible, it was desired to use auric chloride,  $\text{HAuCl}_4$  (or  $\text{AuCl}_3 \cdot \text{HCl}$ ), as the gold sensitizer. This would obviate the need to show that the sodium thiocyanate used to prepare the monovalent complex was photographically inert. Nonetheless, the  $[\text{Au}(\text{SCN})_2]^-$  was tried eventually anyway. Unfortunately, many experiments and much time was wasted trying to achieve a sensitivity increase by Au (following sulfur sensitization) using the level above or levels around it. After  $\text{HAuCl}_4$  failed to give results at the low levels, the thiocyanate complex was tried. The complex did not work either. Even the  $\text{NaSCN}$  was tested alone after sulfur sensitization as a check on its purity. No change was encountered. However, at the low levels of gold, a significant effect was observed at high densities (most pronounced at step 21). While the gold made no significant speed change at the low levels, it markedly reduced the high density areas relative to sulfur alone. To a point, the more gold added, either as  $\text{HAuCl}_4$  or as  $[\text{Au}(\text{SCN})_2]^-$ , the lower the density at the highest exposure (i.e., the position of the toe was not altered but the contrast was

decreased). See Table 7. Much better results were finally obtained using  $\text{HAuCl}_4$  at about 10 times the original suggested level:  $5 \times 10^{-5}$  to  $8 \times 10^{-5}$  moles Au/mole AgX.

#### VI. Testing Equivalency of Gold Sensitization Methods

In order to have a valid test of the effect of stabilizers on gold sensitization, a check had to be made to see if Au+S present from the start of digestion (conventional procedure) would yield a similar speed to the procedure of sulfur sensitization followed by gold sensitization. Table 8 shows that similar speeds were obtainable but the fog level was higher when the gold was added at the start of digestion (for the same Au level).

#### VII. Effect of TAI Stabilizer on Gold Sensitization in an Already-Sulfur-Sensitized Emulsion

After laying the groundwork in the previous experiments, this is the key experiment in the thesis. As shown in Table 5 and by the work of Gingello, MacIntyre, and Carroll,<sup>43,45</sup> TAI added prior to sulfur sensitization entirely prevents any further increase in sensitivity. In order to see if the same effect of TAI also held for gold sensitization, when the emulsion used had already been sulfur sensitized, the following sequence was used. The emulsion was digested for 120 minutes with  $\text{Na}_2\text{S}_2\text{O}_3$  ( $5.0 \times 10^{-5}$  moles/mole AgX) at which time TAI was added (1.0 g/mole Ag). After a 5 minute pause (total time of

125 minutes), gold sensitizer was added, the emulsion was heated an additional 15 minutes, and then coated. As a control, the emulsion was sensitized for 120 minutes with  $\text{Na}_2\text{S}_2\text{O}_3$  ( $5.0 \times 10^{-5}$  moles/mole AgX),  $\text{HAuCl}_4$  was added 15 minutes prior to 120, and TAI was added at 120 minutes. This control should show if the presence of TAI itself had any influence on speed when added to a sulfur and gold sensitized emulsion (compare with experiments in Table 8). Table 9 shows that sensitization from Au did occur in the presence of TAI stabilizer. In addition, fog levels were higher which were also typical of gold sensitization in these experiments. The presence of TAI apparently reduced the sensitivity even when added just before coating (compare to Table 8 without TAI). Even with TAI, however, there was sensitization due to gold.

#### VIII. Determination of the Effect of Digestion Time on Gold Sensitization

From literature sources indicating the usefulness of Au as a final addition in afterripening and as a latensification bath, one might presume that the speed increase due to Au is rapid. However, as a follow up to the experiments in Section VII using Au after TAI, a series of tests were made to determine that heating the emulsion with  $\text{HAuCl}_4$  for 15 minutes was sufficient time to achieve maximum sensitization from Au as had been believed. The data in Table 10 indicate no significant changes when extended gold digestion is given.

## IX. Effect of TAI on Combined S+Au Sensitization

As previous tests had shown that TAI prevented sulfur sensitization but not gold sensitization, the effect of TAI on combined S+Au sensitization made an interesting test. TAI was added to the emulsion and heated for 5 minutes. At 5 minutes, S then Au were successively added and the emulsion was given a 120 minute heating period. As can be observed from Table 11, a large sensitivity increase was obtained although smaller than sulfur only.

## X. Effect of PMT on S+Au Sensitization

In order to observe whether other types of stabilizers interacted with gold sensitization (on a sulfur sensitized emulsion) differently from TAI, a short series of experiments, analogous to those involving TAI, were run using PMT. 1-Phenyl-5-mercaptotetrazole is representative of mercapto stabilizers which form highly insoluble silver salts and which are tightly adsorbed. Since they are strongly adsorbed, they are used in much smaller quantities and are prone to development inhibition. At least some of the speed loss caused by development inhibition may be recovered by using extended development times. In these tests, both the standard 5 minute and a 10 minute development were given. Previous work by Gingello, MacIntyre, and Carroll<sup>43,45</sup> had shown that sulfur sensitization (by  $\text{Na}_2\text{S}$ ) on a single jet emulsion, similar to the one used here,

was retarded but not prevented by PMT. The results shown in Table 12, while somewhat complicated by a general desensitization and/or development inhibition, clearly show that PMT did not interfere with gold sensitization in an already-sulfur-sensitized emulsion. The speeds and fogs for the 10 minute development times look much like the analogous experiments performed with TAI except at a 5 minute development time.

#### XI. Actual Film Speed of the Experimental Emulsion

Though seldom examined, it is often of interest to see how experimental coatings compare with commercial products. Of all characteristics, film speed might be the most revealing. To that end, the coating corresponding to the last entry in Table 9 was examined. This was S then Au, TAI added before coating, higher gold, relative speed 1.84. Using the ANSI criterion for the speed point,  $\frac{0.8}{H}$ , but without regard to contrast, the chemically, but not spectrally, sensitized film had a speed of 10 to a nominal 2850K tungsten source (0.2 sec. exposure). By the same calculation, the film had a speed of 25 to daylight (xenon flash with 1/294 sec. exposure time).

#### XII. Additional Comments on the Interaction of Gold and Sulfur Sensitizers

Since the time of the original literature search (1978) and the completion of experiments (February, 1979), some

additional information has become available in the literature which would have affected the design of the experiments and which will affect the interpretation of the experimental results. The new data concerns the effect of the presence of gold on the rate of increase of photographic sensitivity in emulsions chemically sensitized with S+Au. At the time of the experimental work for this thesis, there were apparently only four references relating to this topic. Faelens<sup>21</sup>, using a fine grain, gelatin-free AgBr sol, presented evidence that the presence of gold caused an increase in the rate of sulfide formation from sulfur sensitizers. This was not judged to be a problem because the system was gelatin-free and because it had been previously shown that there is no unique quantity of silver sulfide at optimum digestion.<sup>7</sup> The time of digestion until optimum sensitivity was not mentioned as being changed by either reference. Moisar<sup>58</sup> showed that the presence of gold accelerates thiosulfate breakdown at cubic faces, but not at octahedral faces, of monodisperse AgBr emulsions. The emulsion used in the present work presumably consists largely of doubly twinned octahedra. Locker<sup>22</sup> and Pitt, Rachu, and Sahyun<sup>59</sup> showed an increase in the rate of sensitization in the presence of gold for a cubic AgBrI emulsion. Again, absolute digestion times until optimum sensitivity were not given by either reference.

A recent paper by Farnell and Solman<sup>20</sup> (1980) indicates that a component of the speed increase attributable to gold in S+Au sensitization is due to an increase in the rate of sulfide deposition using 8 types of AgBr emulsions. Pitt, Rachu, and Sahyun<sup>60</sup> (1981) have just shown that the presence of gold, as well as its level, affects the time until optimum sensitivity. With their system, once optimum speed is reached in the presence of gold, a long, unchanging speed plateau (in terms of digestion time) is reached. They do not show fog levels vs. digestion time.

This information is relevant to this work because the optimum speed of an emulsion, first sensitized only with sulfur, to optimum, and then sensitized with gold, was compared with the speed reached by the emulsion sensitized with the same levels of S and Au added at the start of digestion, for the same times of ripening. This means that the emulsion digested with S+Au added at the start of chemical sensitization may have been slightly over-digested when compared with the sequential S then Au experiment. However, as Pitt<sup>60</sup> et al. show a speed plateau, results here should still be totally valid. Fog levels probably do not level off and would be expected to be higher for the experiment where S+Au was added at the start of digestion. This was precisely the case for the fog levels found in these experiments.



## CONCLUSIONS

1. In agreement with the literature, full S+Au sensitization could be achieved by simultaneous introduction of the sensitizers and heating or by adding gold to an already sulfur sensitized emulsion.
2. Gold sensitization, by either method above, was retarded but not prevented by the presence of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene, as opposed to the action of the stabilizer on sulfur sensitization.
3. 1-Phenyl-5-mercaptotetrazole, used in quantities sufficient to cause some inhibition of development, retards but does not inhibit sensitization by gold which follows full sulfur sensitization.
4. Gold sensitization may be achieved without the long times or high temperatures necessary for sulfur sensitization. This may indicate that its incorporation is due to a direct chemical reaction. 6-Methyl-4-hydroxy-1,3,3a,7-tetrazaindene does not prevent chemical reaction of sulfur sensitizers with silver halide and it is unlikely that it would in the case of gold. This may suggest that gold sensitization does not involve a rearrangement or other secondary process with which a stabilizer may interfere.

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## APPENDIX A

### Tables

## PREFACE TO DATA TABLES

"S" is used to indicate sensitization with sulfur ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )

"Au" is used to indicate sensitization with gold ( $\text{HAuCl}_4$ )

"S+Au" is used to indicate combined sensitization without regard to the method the sensitizers were added

All sensitizations, heating, and holding periods were done at 55°C.

The starting pH and pAg for the treatments were the same as those of the primitive emulsion: pH 6.3, pAg 8.8 (40°C)

Sensitizer and Stabilizer levels per mole AgX (unless otherwise stated)

$\text{HAuCl}_4$	$5.0 \times 10^{-5}$ mole
$\text{Na}_2\text{S}_2\text{O}_3$	$5.0 \times 10^{-5}$ mole
TAI (sodium salt)	1.0 gram
PMT	50 mg

Times of Digestion for Stabilizers and Sensitizers (unless otherwise stated)

$\text{HAuCl}_4$	15 minutes
$\text{Na}_2\text{S}_2\text{O}_3$	120 minutes
TAI (sodium salt)	5 minutes
PMT	5 minutes

Relative Speed: Calculated as the log exposure necessary to produce a density of 0.1 above base plus fog density, relative to the unsensitized emulsion which was assigned a speed of 0.0.

Development: Kodak DK-50 developer for 5 minutes (unless otherwise stated) was used with continuous agitation. Temperature was held in the range of 67.5 to 68.0°F.

TABLE 1

## Preparation of the Neutral, Single Jet, AgBrI Emulsion

Batch Size: 0.2 moles Ag

Make Temperature:  $64 \pm 1^\circ\text{C}$

Run Time: 32 minutes, 20 seconds

Agitation: homogenizer turbine

(several thousand rpm)

Jet Solution: 900 ml  $\text{H}_2\text{O}$

33.98 g  $\text{AgNO}_3$  (0.2000 moles)

907 ml total volume

0.2206 N

Vessel Contents (Starting): 660 ml  $\text{H}_2\text{O}$

26.00 g of 98.65% KBr (0.2155 moles)

1.01 g of 98.75% KI (0.00601 moles)

8.0 g phthalated gelatin

677 ml total volume

0.2215 moles total halide

0.3272 N halide

1.2% gelatin

2.71 mole % iodide

Final Volume: 1575 ml

Final Halide Concentration: 0.01365 N (calculated)

pBr = 1.86

pAg = 9.75 ( $40^\circ\text{C}$ )

Ag/X Ratio: 1/1.1075 as moles

(10.75 mole % excess halide)

TABLE 1 (continued)

Gelatin/ $\text{Ag}^\circ$ Ratio:	0.37 g gelatin/g $\text{Ag}^\circ$ or 39.9 g gelatin/ mole Ag
Physical Ripening:	22 minutes at 65°C 11.69 g of 98.65% KBr (0.09690 moles) added at end of jetting 0.0215 moles halide already present +0.09690 added = 0.1184 moles total 0.1184 moles total halide in 1575 ml = 0.07517 <u>N</u> halide pBr = 1.12, pAg = 10.49 (40°C) (calculated)
Coagulation:	108 ml of 0.1017 <u>N</u> $\text{H}_2\text{SO}_4$ and refrigerated
Redispersion:	Coagulum mixed with redispersing solution at 40°C
Redispersing Solution:	800 ml of 0.001540 <u>N</u> KBr (pAg = 8.8) + 48.0 g inert bone gelatin + 14.2 ml 0.4907 <u>N</u> NaOH
Final Primitive Emulsion:	0.224 moles Ag/liter of emulsion or 14.9 mg $\text{Ag}^\circ$ /g emulsion 6.28% gelatin (gel/Ag = 2.32/1) pAg = 8.8, pH = 6.2 to 6.5 (40°C)

TABLE 2

## Summary of Analyses

0.1017 N $\text{H}_2\text{SO}_4$ :	titrated against 0.1000 N NaOH from an Acculate concentrate (Anachemia Chemicals Ltd.) to a bromthymol blue end point (average of six titrations). Approximately 8 liters prepared.
0.4907 <u>N</u> NaOH:	titrated against 0.1017 N $\text{H}_2\text{SO}_4$ (above) to a bromthymol blue end point (average of 5 titrations). Approximately 6 liters prepared.
98.65% KBr:	titrated against 0.0500 <u>N</u> $\text{AgNO}_3$ potentiometrically using an Ag/AgBr electrode and an SCE reference (average of 4 titrations).
98.75% KI:	titrated against 0.0500 <u>N</u> $\text{AgNO}_3$ potentiometrically using an Ag electrode and an SCE reference (average of 4 titrations). $\text{AgNO}_3$ was same as used in the emulsion.
Phthalated Gelatin:	titrated against 0.1017 N $\text{H}_2\text{SO}_4$ . Out of 4 titrations, it appeared that the first permanent turbidity occurred at about pH 4.4 and no more gelatin coagulated below a pH of 4.0. The isoelectric point is, apparently, at about pH 4.0. A plot of the titration curve has such a shallow inflection point that it was not very useful for isoelectric point determination.

TABLE 3

Heating of Primitive Emulsion (Gelatin Test) 55°C

Digestion Time	Rel. Speed	Base & Fog Density	Step 21 Density*
0 min.	0	0.03	0.52
90 min.	0.07	0.03	0.60
180 min.	0.12	0.03	0.63
300 min.	0.12	0.03	0.67

\* No auxiliary filters: highest attainable exposure but not Dmax

TABLE 4

Sulfur Sensitization Level Test

A 2.5x10 <sup>-5</sup> moles Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> per mole Ag			B 5.0x10 <sup>-5</sup> moles Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> per mole Ag		
Digestion Time	Rel. Speed	Base & Fog	Digestion Time	Rel. Speed	Base & Fog
0 min.	0	0.03	0 min	0	0.03
30 min.	0.12	0.03	45 min.	0.28	0.03
60 min.	0.34	0.03	90 min.	1.07	0.03
90 min.	0.53	0.03	135 min.	1.43	0.03
120 min.	0.71	0.03	180 min.	1.65	0.07
150 min.	0.93	0.03	225 min.	1.51	0.21
210 min.	1.20	0.05			



TABLE 5

## TAI Stabilization Tests on Sulfur Sensitization

Treatment*	Total Digestion Time	Rel. Speed	Base & Fog
S only	150 min.	1.53	0.10
S then TAI at 140 min.	180 min.	1.48	0.15
S only	120 min.	1.47	0.04
S then TAI at 120 min.	150 min.	1.40	0.04
S then TAI at 120 min.	180 min.	1.38	0.04
TAI then S at 5 min.	125 min.	-0.11	0.03
S then TAI at 120 min.	120 min.	1.53	0.04
		1.45	0.04
		1.53	0.08

S =  $5 \times 10^{-5}$  moles  $\text{Na}_2\text{S}_2\text{O}_3$ /mole AgX

TABLE 6

## Speed/Fog vs. Digestion Time for Sulfur Sensitization

$\text{Na}_2\text{S}_2\text{O}_3$  at  $5.0 \times 10^{-5}$  moles/mole AgX

Digestion Time	Rel. Speed	Base & Fog
90 min.	1.33	0.03
120 min.	1.50	0.04
150 min.	1.53	0.10

TABLE 7

## Contrast Lowering Effect of Low Au Levels

Treatment*	Rel. Speed	Base & Fog	Density at Step 21
No Au	1.46	0.04	3.18
$3 \times 10^{-7}$ m/m $\text{Au}^{+3}$	1.44	0.04	2.81
$7.5 \times 10^{-7}$ m/m $\text{Au}^{+3}$	1.50	0.05	2.82
$1.5 \times 10^{-6}$ m/m $\text{Au}^{+3}$	1.47	0.04	2.25
$3.0 \times 10^{-6}$ m/m $\text{Au}^{+3}$	1.47	0.04	1.92
$6.0 \times 10^{-6}$ m/m $\text{Au}^{+3}$	1.41	0.04	2.17
$6.0 \times 10^{-6}$ m/m $\text{Au}(\text{SCN})_2^-$	1.44	0.05	2.13
$1.2 \times 10^{-5}$ m/m $\text{Au}^{+3}$	1.35	0.04	2.19
$1.2 \times 10^{-5}$ m/m $\text{Au}(\text{SCN})_2^-$	1.50	0.05	2.14
$2.0 \times 10^{-5}$ m/m $\text{Au}^{+3}$	1.65	0.07	2.84
$3.0 \times 10^{-5}$ m/m $\text{Au}^{+3}$	1.79	0.09	3.83
$5.0 \times 10^{-5}$ m/m $\text{Au}^{+3}$	1.96	0.14	3.92
$8.3 \times 10^{-5}$ m/m $\text{Au}^{+3}$	1.96	0.26	3.73

\* digested with  $5.0 \times 10^{-5}$  moles  $\text{Na}_2\text{S}_2\text{O}_3$ /mole AgX for 120 minutes; Au added 15 minutes prior to 120 min.; amounts shown are moles Au/mole AgX.

TABLE 8

## Equivalency of Gold Sensitization Methods

Treatment*	moles Au/ mole AgX	Rel. Speed	Base & Fog
S then Au	$5.0 \times 10^{-5}$	1.93	0.07
		1.96	0.14
S+Au from start	$5.0 \times 10^{-5}$	1.90	0.22
S then Au	$8.3 \times 10^{-5}$	1.96	0.24

\* digested with  $5.0 \times 10^{-5}$  moles  $\text{Na}_2\text{S}_2\text{O}_3$ /mole AgX for 120 minutes; for "S then Au", Au was added 15 min. prior to 120 min. in order to keep total sulfur sensitization time the same.

TABLE 9

Effect of TAI Stabilizer on Gold Sensitization

Treatment	moles Au/ mole AgX	Rel. Speed	Base & Fog
S then TAI then Au* (first emulsion)	$5.0 \times 10^{-5}$	1.67 1.64 1.67 1.64	0.06 0.05 0.06 0.05
S then TAI then Au* (second emulsion)	$5.0 \times 10^{-5}$	1.76 1.74	0.07 0.09
S then TAI then Au* (higher gold)	$8.3 \times 10^{-5}$	1.79 1.79	0.10 0.06
S then Au, TAI added before coating**	$5.0 \times 10^{-5}$	1.79 1.79 1.81	0.07 0.09 0.08
S then Au, TAI added before coating (higher gold)**	$8.3 \times 10^{-5}$	1.85 1.84	0.18 0.12

All tests: S level =  $5.0 \times 10^{-5}$  moles/mole AgX, TAI level = 1.0 g/  
mole AgX

\* Emulsion heated with S for 120 minutes; TAI added at 120 min.  
and held 5 min., Au added at 125 min. and heated for an  
additional 15 min.

\*\* Emulsion heated with S for 120 min., Au added 15 minutes prior  
to 120 min., TAI added at 120 min.

TABLE 10

Effect of Au Digestion Time on Au Sensitization After TAI

Treatment	Au Digestion Time	Rel. Speed	Base & Fog
S then TAI then Au*	15 minutes	1.76	0.07
	15 minutes	1.74	0.09
	30 minutes	1.75	0.09
	60 minutes	1.70	0.06

\* Emulsion heated with S for 120 minutes, TAI added at 120 minutes and held 5 min., Au added at 120 min. and digested for the times listed above.

All tests: S Level =  $5.0 \times 10^{-5}$  moles/mole AgX, TAI level = 1.0 g/mole AgX

Table 11

Effect of TAI on Combined S+Au Sensitization

Treatment*	Rel. Speed	Base & Fog
TAI for 5 min., then S+Au for additional 120 minutes	1.35	0.06
TAI for 5 min., then S only for additional 120 min.	-0.11	0.03

\* TAI level = 1.0 g/mole AgX; S, Au =  $5 \times 10^{-5}$  moles/mole

TABLE 12

Effect of PMT on S+Au Sensitization

Treatment *	moles Au/ mole AgX	RELATIVE SPEED		BASE & FOG	
		5 min. dev.	10 min. dev.	5 min. dev.	10 min. dev.
S then PMT before coating	none	1.38	1.50	0.04	0.05
S then Au then PMT	$5.0 \times 10^{-5}$	1.62	1.81	0.06	0.13
	$8.3 \times 10^{-5}$	1.67	1.88	0.19	0.30
S then PMT then Au	$5.0 \times 10^{-5}$	1.50	1.74	0.08	0.08
	$8.3 \times 10^{-5}$	1.60	1.81	0.06	0.11
		1.65	1.93	0.16	0.21

All tests:  $S = 5.0 \times 10^{-5}$  moles  $\text{Na}_2\text{S}_2\text{O}_3$ /mole AgX,

PMT = 50 mg/mole AgX

\* The sulfur digestion was 120 minutes for all cases - for S then Au then PMT, Au was added 15 min. prior to 120 min., PMT was added at 120 min. - for S then PMT then Au, PMT was added at 120 min. and held for 5 min., Au was added at 125 min. and the emulsion was heated an additional 15 min.

## APPENDIX B

### Figures

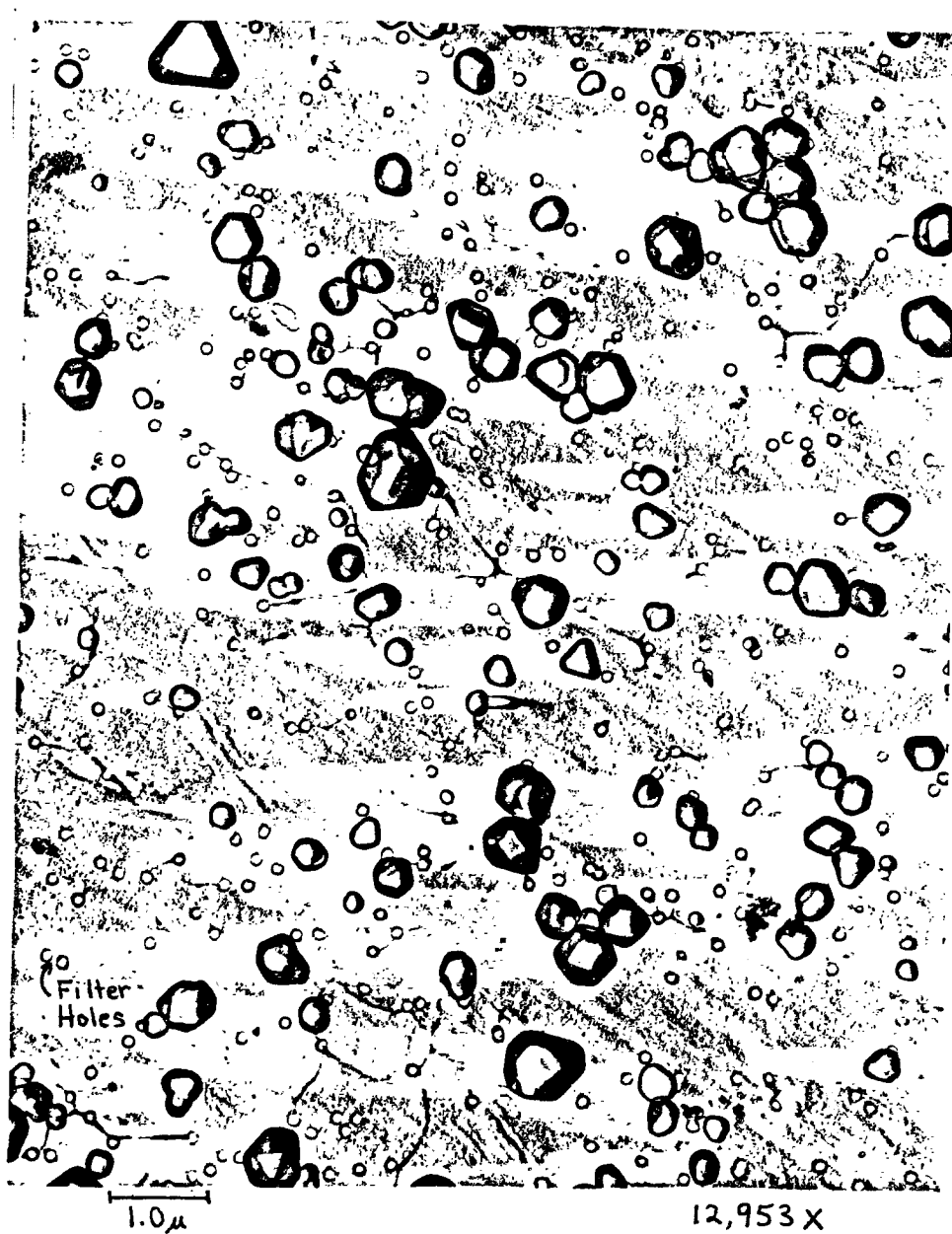


FIGURE 1

Electron Micrograph of Experimental Single Jet Emulsion

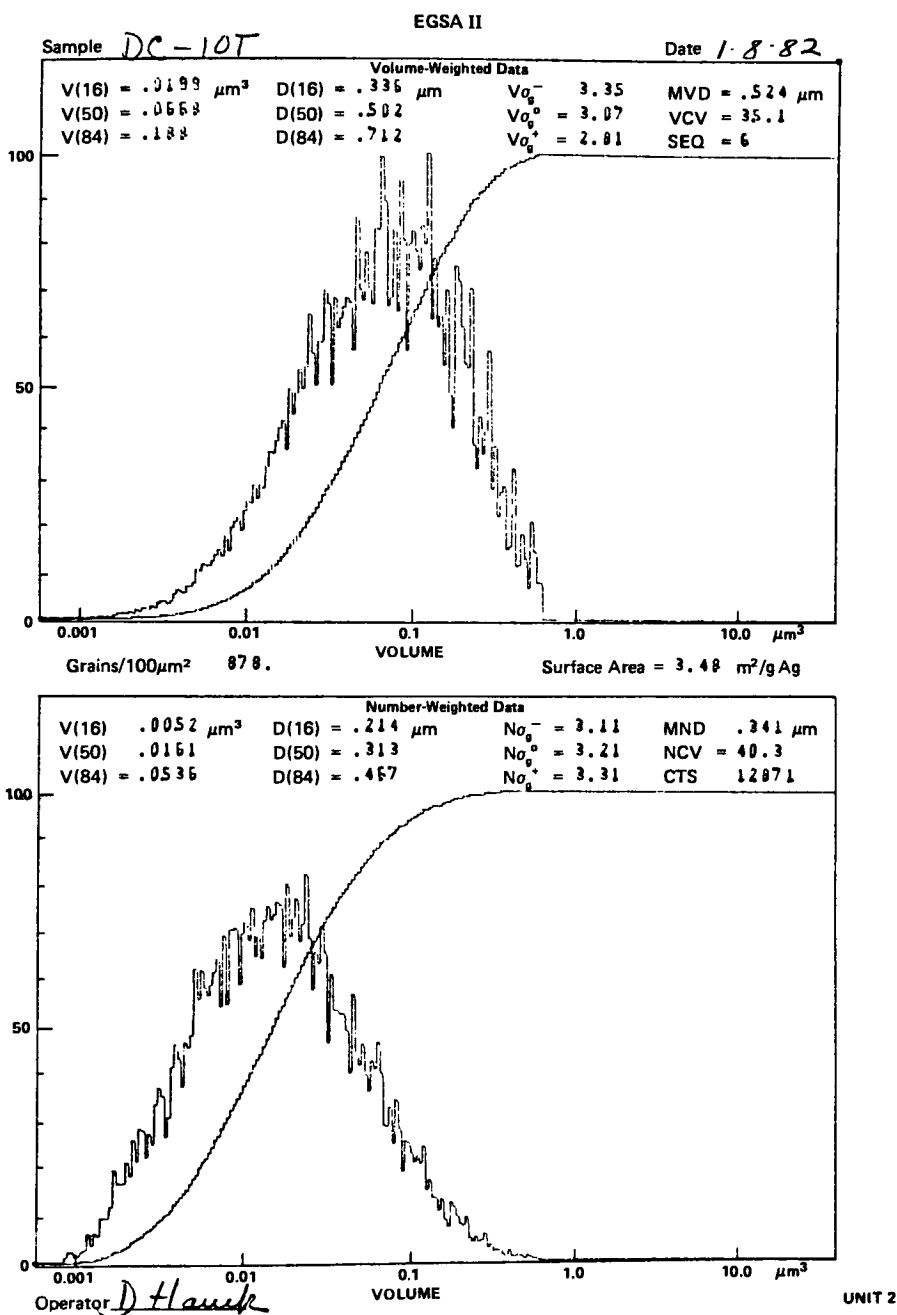


FIGURE 2

Grain Size Frequency Distributions of Experimental Emulsion



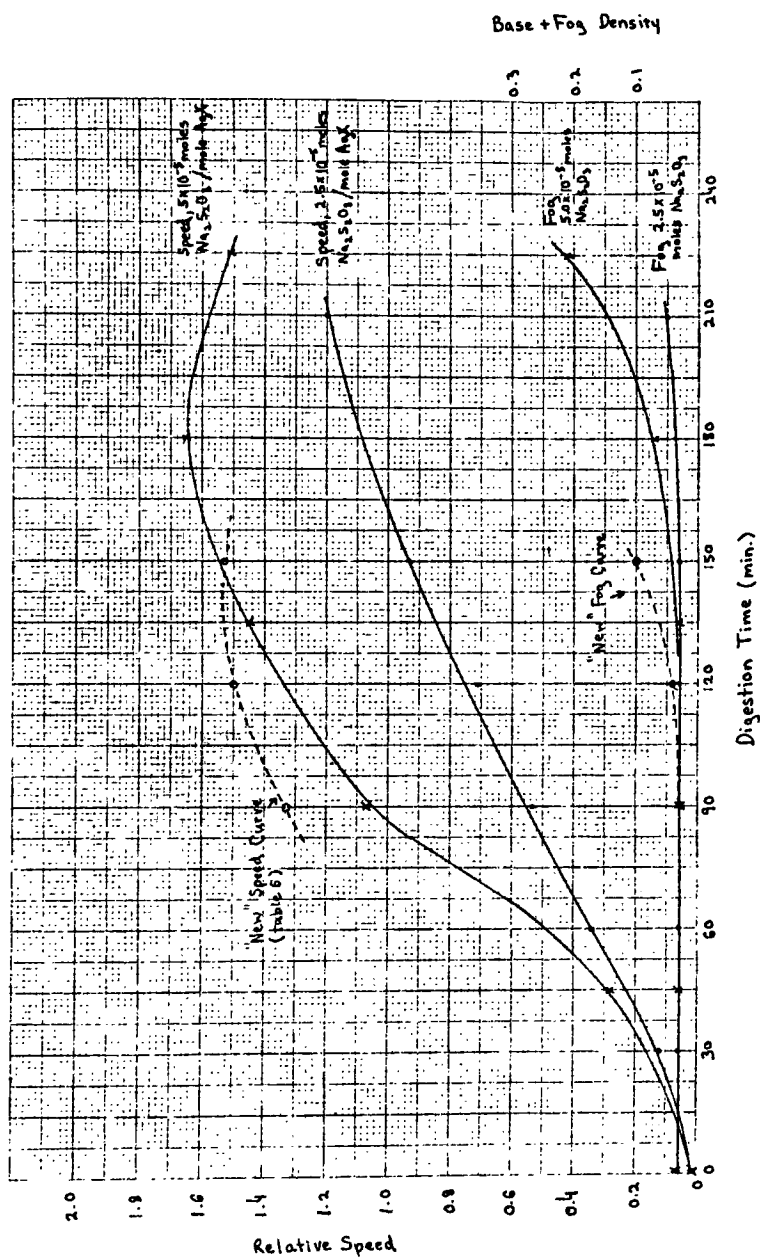


FIGURE 3

SPEED/FOG VS. DIGESTION TIME FOR SULFUR SENSITIZATION

POLAROID CORPORATION **RECORDING CHART** GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK No GC 13361-SP

TEMP 68°F TEST

D MAX \_\_\_\_\_  
D MIN \_\_\_\_\_  
SLOPE \_\_\_\_\_  
SPEED \_\_\_\_\_

GAP \_\_\_\_\_  
IMB \_\_\_\_\_  
ROLLERS \_\_\_\_\_  
DENSITOMETER \_\_\_\_\_  
DATE \_\_\_\_\_ BY \_\_\_\_\_

NEG \_\_\_\_\_  
POD Kodak DK-50 for 5 min \_\_\_\_\_  
SHEET \_\_\_\_\_  
SENSITOMETER Kodak Model 101 \_\_\_\_\_  
TARGET Kodak No. 2 Step Tablet \_\_\_\_\_  
EXPOSURE 21.5 lux sec. (mcs), 0.1 sec. \_\_\_\_\_

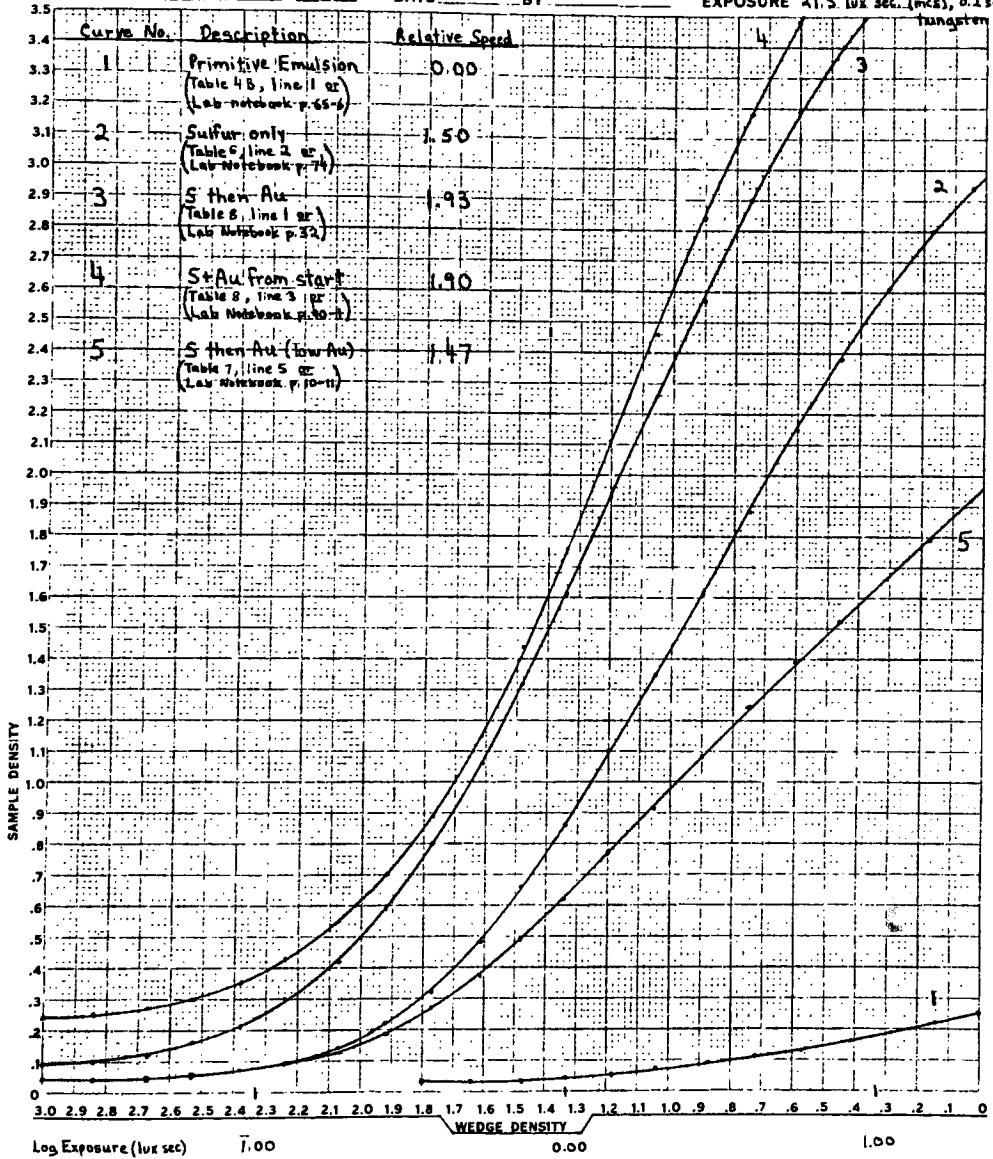


FIGURE 4

D-Log H Curves of the Different Types of Chemical Sensitization

POLAROID CORPORATION **RECORDING CHART** GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK no. GC 13361-SP

TEMP 68°F

TEST

D MAX \_\_\_\_\_  
D MIN \_\_\_\_\_  
SLOPE \_\_\_\_\_  
SPEED \_\_\_\_\_

GAP \_\_\_\_\_  
IMB \_\_\_\_\_  
ROLLERS \_\_\_\_\_  
DENSITOMETER \_\_\_\_\_  
DATE \_\_\_\_\_ BY \_\_\_\_\_

NEG \_\_\_\_\_  
POD Kodak DK-50 for 5 min. \_\_\_\_\_  
SHEET \_\_\_\_\_  
SENSITOMETER Kodak Model 101 \_\_\_\_\_  
TARGET Kodak No. 2 Step Tablet \_\_\_\_\_  
EXPOSURE 21.5 lux sec. (mcs) 0.2 sec. (mcs) \_\_\_\_\_

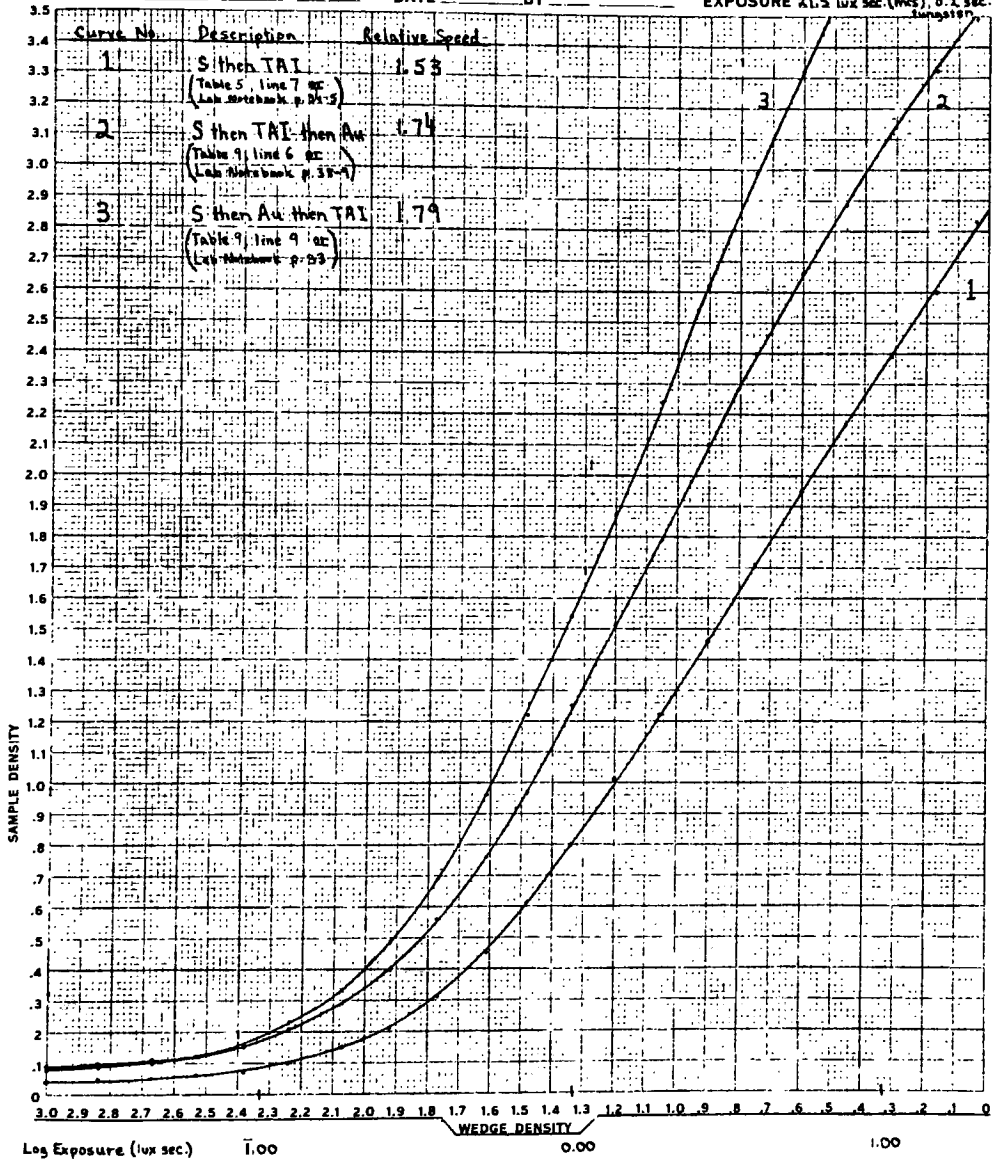


FIGURE 5

D-Log H Curves of the Effect of TAI on Chemical Sensitization

POLAROID CORPORATION **RECORDING CHART** GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK No. GC 13361-SP

TEMP 68°F

TEST

D MAX \_\_\_\_\_  
D MIN \_\_\_\_\_  
SLOPE \_\_\_\_\_  
SPEED \_\_\_\_\_

GAP \_\_\_\_\_  
IMB \_\_\_\_\_  
ROLLERS \_\_\_\_\_  
DENSITOMETER \_\_\_\_\_  
DATE \_\_\_\_\_ BY \_\_\_\_\_

NEG \_\_\_\_\_  
POD Kodak DK-50 for 5 min. \_\_\_\_\_  
SHEET \_\_\_\_\_  
SENSITOMETER Kodak Model 101 \_\_\_\_\_  
TARGET Kodak No. 2 Step Tablet \_\_\_\_\_  
EXPOSURE 21.5 lux sec. (mcs), 0.2 sec. \_\_\_\_\_

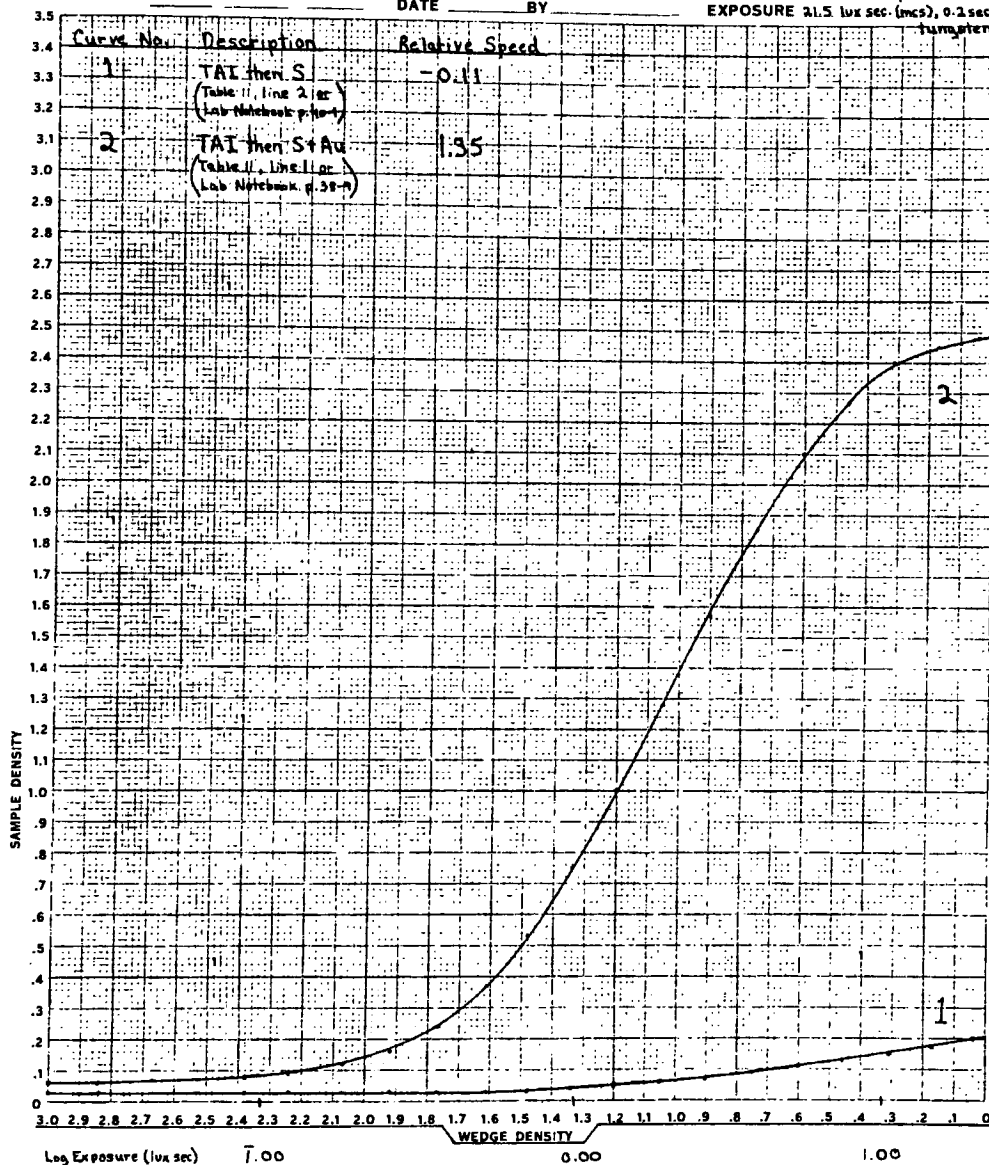


FIGURE 6

D-Log H Curves of TAI Before S and Before S+Au

POLAROID CORPORATION **RECORDING CHART** GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK NO GC 13361-SP

TEMP 68°F TEST

D MAX \_\_\_\_\_  
D MIN \_\_\_\_\_  
SLOPE \_\_\_\_\_  
SPEED \_\_\_\_\_

GAP \_\_\_\_\_  
IMB \_\_\_\_\_  
ROLLERS \_\_\_\_\_  
DENSITOMETER \_\_\_\_\_  
DATE \_\_\_\_\_ BY \_\_\_\_\_

NEG \_\_\_\_\_  
POD. Kodak DK-50 for 10 min.  
SHEET \_\_\_\_\_  
SENSITOMETER Kodak Model 10L  
TARGET Kodak No. 3 Step Tablet  
EXPOSURE 21.6 lux sec (mcs), 0.2 sec  
1000 ft/min

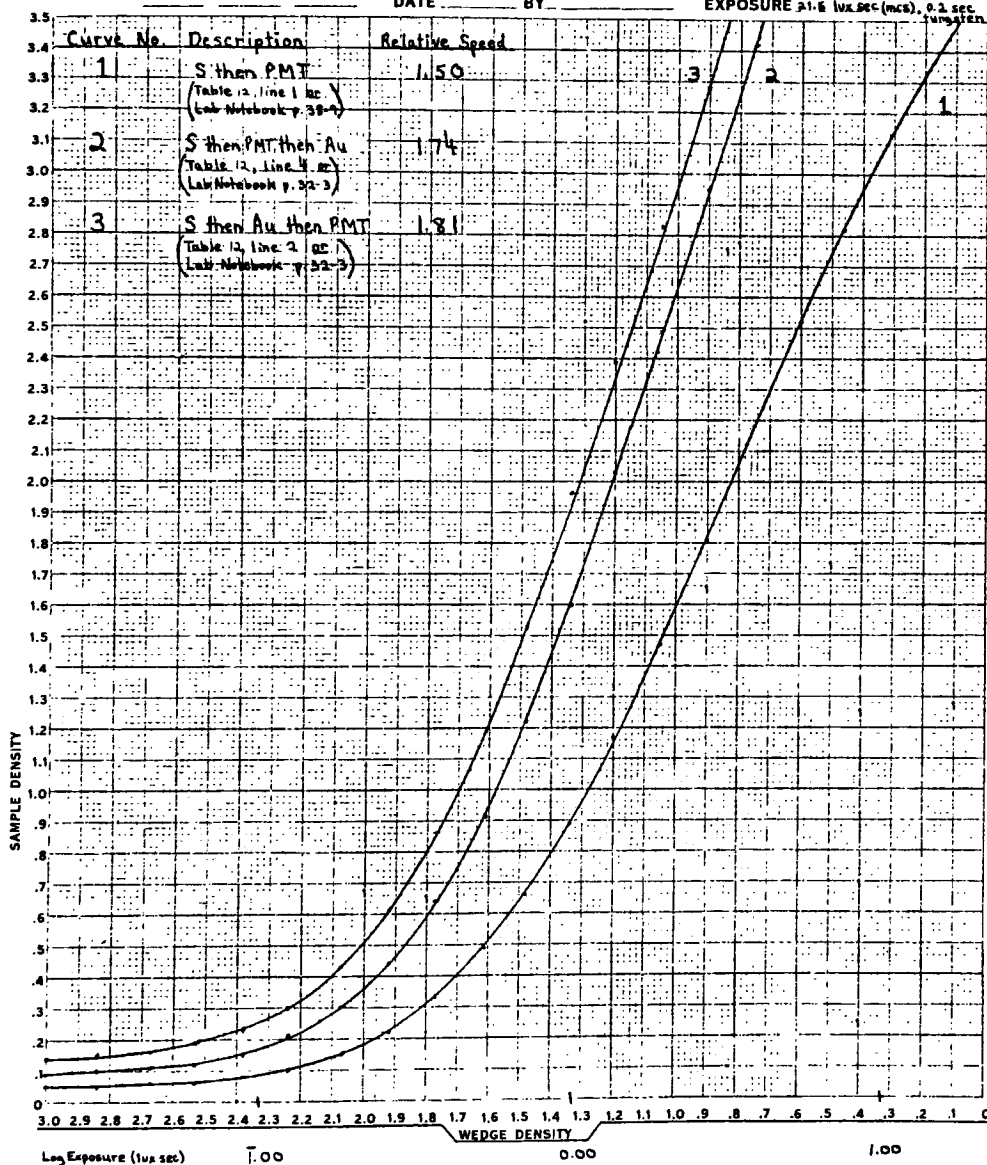


FIGURE 7

D-Log H Curves of the Effect of PMT on  
Chemical Sensitization



## VITA

Douglas E. Corbin, a U.S. citizen, was born on May 1, 1952 in Des Moines, Iowa. He moved to Santa Barbara, California in 1963 with his family. His education there included an A.A. in physical science from Santa Barbara City College in 1972 and a B.S. in chemistry from the University of California at Santa Barbara in 1974. Seeking a way to combine studies in chemistry and photography, he was enrolled in the M.S. program in photographic science and instrumentation at the Rochester Institute of Technology, Rochester, New York from 1975 to 1979 and obtained the degree in 1982. He has been employed by the Polaroid Corporation, Waltham, Massachusetts, since 1979 and works in the areas of silver halide emulsion research and product development. Currently single, he resides in Billerica, Massachusetts.